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(54) TOOTH BLEACHING COMPOSITIONS AND METHOD OF BLEACHING DISCOLORED TOOTH

(57) The bleaching compositions of discolored teeth comprise titanium dioxide initiating photocatalyst action with light irradiation, chemical compounds generating hydrogen peroxide in an aqueous solution and thickening agents. Further the bleaching methods of discolored teeth comprising applying the bleaching composition onto the surface area of the teeth and then initiating pho-

tocatalyst action by irradiating the applied surfaces area with light. Therefore, the present invention shows remarkable bleaching results due to easy application of the compositions onto discolored teeth and keeping the original activity of the photocatalyst without its deterioration.

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Description

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TECHNICAL FIELD

[0001] The present invention relates to methods for bleaching and removing colored sediment on teeth by photocatalytic action, and tooth bleaching compositions for the methods. More particularly, the present invention relates to methods for bleaching the discolored teeth by applying the bleaching composition, comprising certain compounds having photocatalytic activity, onto the discolored teeth and then irradiating the applied area with light, and also the present invention relates to the bleaching compositions for the bleaching methods.

BACKGROUND ART

[0002] Recent year, there have been increasing demand for esthetic improvements of teeth such as improvements of contours, alignment and integrity of teeth in dental therapy. In particular, there have been more cases of young women desiring such dental therapy so as to whitening teeth as an important element of beauty. Generally, the cause of dental discoloration and pigmentation or stain falls into the two categories: (1) extrinsic causes such as sedimentation of colored materials (tobacco, tea, etc.), pigment generating bacteria, discoloration of filling materials (primarily composite resins) and metal salts (primarily amalgam, silver nitrite, and ammonia silver); and (2) intrinsic causes such as aging, chemicals or medicine (ex. fluorine and tetracyclines), dysmmetabolism and hereditary, and dental injuries. The National Health Insurance is applicable to bleaching methods for, the latter, discolored teeth intrinsically.

[0003] Several methods have been proposed as methods for esthetic improvement of discolored teeth, among which bleaching may be considered as a highly effective method for the preservation of dentine if a suitable method for each decease case would be selected and carried out properly, although there may be some cases of color reversion. Bleaching is basically a method for decolorizing colored materials through a chemical reaction. In the past, there were various reports of bleaching agents comprising a variety of chemicals based on vital bleaching and non-vital bleaching as well as bleaching methods using such agents.

[0004] The following are typical examples:

(1) Bleaching method using 30% H₂O₂ as a chemical combining light and heat in parallel.

This is a method in which strips of gauze soaked in 30% $\rm H_2O_2$ are placed on the front surfaces of teeth and are irradiated for 30 minutes from the left and right by using two 500W photographic lamps. In this method, the lamps are set as close to the gauze as possible and the $\rm H_2O_2$ should be replenished about every 5 minutes so as to prevent them from drying.

(2) Bleaching method using 30% H₂O₂ as a chemical combining high frequency current in parallel.

This is a method in which strips of gauze soaked in $30\% \, H_2O_2$ are placed on the front surface of teeth and high frequency current is delivered for one second with a spoon-shaped tip of a frequency scalpel and is not delivered for 8 second. The operation should be repeated 6 to 8 times and H_2O_2 should be replenished to keep them wet during the treatment.

(3) Bleaching method using a paste comprising Aerosol (fine silica powder) mixed with 35% $\rm H_2O_2$ and the paste is applied.

This is a method in which the paste is applied onto the surfaces of the etched teeth, 15 minutes later the teeth are rinsed with water and then polished. The method gives a highly bleaching result without using light or heat as Aerosol serves as a moisturizing material to prevent the bleaching agent from drying out and also enhances the bleaching effects. The 35% $\rm H_2O_2$ should be handled with care due to its highly corrosive property.

(4) Bleaching method using a paste (Shofu Hi-Lite: tradename), obtained by kneading a 35% $\rm H_2O_2$ solution and a powder comprising potassium sulfate, manganese sulfate, silicon dioxide or the like, as a chemical.

This is a method in which the paste is placed on the front surfaces of teeth and worked for 10 minutes or irradiated it with light for 3 minutes by applying a visible light ray radiation device. An advantage of the method is as follows: The paste shows a light green immediately after the kneading and then turn yellow by the light irradiation. If the paste turns dark-brown immediately after the kneading, this indicates that the bleaching effects of the liquid have diminished. However there is the same disadvantage mentioned the above due to the use of 35% H₂O₂. (5) Bleaching method using a mixture of 1 ml of 30% HCl. 1 ml of 30% H₂O₂, and 0.2ml of diethyl ether as chemical

(5) Bleaching method using a mixture of 1 ml of 30% HCl, 1 ml of 30% $\rm H_2O_2$, and 0.2ml of diethyl ether as chemical (Improved Machines bleaching).

In this method, the mixture is allowed to act for 5 minutes on tooth surfaces, and then the teeth are polished for 15 minutes under light pressure using a polishing disc. The treatment is repeated 3 times, then they are neutralized with 5.25% NaOCI and the teeth are thoroughly rinsed with water (Oral Surg., 26: 871-878(1968), J. Am. Dent. Assoc., 87: 1329(1973)). In this method, since the paste may scatter into the patient's eyes, it is, necessary to protect them from it adequately.

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- (3) Tooth bleaching composition according to above (1) or (2), wherein the chemical compound is selected from the group consisting of hydrogen peroxide, perborate, percarbonate, persulfate, perphosphate, calcium peroxide, magnesium peroxide and urea peroxide,
- (4) Tooth bleaching composition according to any one of above (1) to (3), wherein the thickening agent is layer-structure clay minerals, phosphoric acid or phosphate,
- (5) Tooth bleaching composition according to above (4), wherein the thickening agent is an inorganic clay mineral selected from the group consisting of saponite, montmorillonite, stevensite, hectonite, smecnite, nacrite and sepolite
- (5) Tooth bleaching composition according to above (4), wherein phosphate is tetra-sodium pyrophosphate,
- (7) Tooth bleaching composition according to any one of above (1) to (6), wherein the content of the chemical composition by dropping peroxide in an aqueous solution is 35 % by weight or less.
- (8) More the reaching discolored teeth by applying the tooth bleaching composition onto the surfaces of the discolored teeth by applying the tooth bleaching composition onto the surfaces of the discolored teeth by applying the tooth bleaching composition onto the surfaces of the discolored teeth by applying the tooth bleaching composition onto the surfaces of the discolored teeth by applying the tooth bleaching composition onto the surfaces of the discolored teeth by applying the tooth bleaching composition onto the surfaces of the discolored teeth by applying the tooth bleaching composition onto the surfaces of the discolored teeth by applying the tooth bleaching composition onto the surfaces of the discolored teeth by applying the tooth bleaching composition onto the surfaces of the discolored teeth by applying the applying the tooth bleaching composition onto the surfaces of the discolored teeth by applying the applying the
- (9) Morth 1: Aug. 10 hg/tc above (8), wherein the wavelength of the irradiating light is 300 nm or longer.

PREFERROR AND COMENT OF THE INVENTION

[0012] Schallte achieve the objectives mentioned above, the present invention utilizes titanium dioxide initiating photocalaryte action by light tradiation and tooth bleaching compositions containing a thickening agent, thereby remarkable results of discolared teeth bleaching as well as improved application ability during treatment are brought in. In the present invention, it is defined that the term of discoloration has broad meanings including pigmentation and stain. [0013] In preferred embodiments, the tooth bleaching compositions of the present invention are composed of solution or paste comprising titanium dioxide, a chemical compound generating hydrogen peroxide in aqueous solution and a thickening agent. Although any types of titanium dioxide, without regard to its form or property, is possible to use for the invention only if it initiales the photocatalytic action, the anatase-type, the rutile-type and the brookite-type are preferred. Further the transum oxide improved its affinity to a tooth surface by coating the surface of the titanium dioxide with calcium phosphate is probable to use. Furthermore, the titanium dioxide of which photocatalytic activity is improved by depositing platinum on it or the titanium dioxide treated by plasma and the like which initiate the photocatalytic action by visible light is probable to use. Titanium dioxides of powder-type or sol-type obtained from dispersing it into a medium such as water can be employed too. The titanium dioxide of the particle diameter 1 to 500 nm is suitable for the use, further the particle giameter 5 to 200 nm is preferable to it. A small amount of the titanium dioxide content effects reasonably however, a very small amount of the titanium dioxide content takes longer time so as to obtain reasonable results which depends on the intensity of tooth discoloration. On the other hand, too high content of it inversely causes lowering the bleaching effects due to titanium dioxide's low light penetration. Therefore, the preferred content of titanium dioxide in the bleaching compositions is 0.001 to 10 % by weight. The content of 0.01 to 1 % by weight is more preferable, and the content of 0.01 to 0.1% by weight is further more preferable.

[0014] Any chemical compound, if it generates hydrogen peroxide by making its aqueous solution, is to be used for the present invention. The chemical compounds generating hydrogen peroxide in a aqueous solution suitable for the present invention is, for example, hydrogen peroxide, perborate, percarbonate, persulfate, perphosphate, calcium peroxide, magnesium peroxide, urea peroxide, and the like. Hydrogen peroxide is preferable. The very small amount of the chemical compounds generating hydrogen peroxide mentioned above are able to show remarkable bleaching results by comparing with conventional bleaching compounds. Therefore, the content of the chemical compound in the bleaching compositions is preferably 35% by weight or less, more preferably 10% by weight or less and further more preferably 5 to 10 % by weight. If the content is higher than the maximum range, there is no much difference in the bleaching results but it has disadvantage in view of safety.

[0015] Aqueous type of the thickening agents is preferred for the thickening agents being used for the present invention. Aqueous organic polymer, aqueous emulsion, clay minerals, phosphate and, the like are the examples of the aqueous type of the thickening agents. In case of the aqueous type of the thickening agent comprising an organic compound as its main constituent, active oxygen generated by photocatalyst action of titanium dioxide is not only used for the tooth bleaching but also consumed for the reaction with the thickening agents. Therefore, it is preferred to use clay minerals and inorganic compounds such as phosphoric acid, phosphate and so on in the present invention. It is furthermore preferred to use layer-structure inorganic clay minerals, phosphoric acid or phosphate.

[0016] Inorganic clay minerals are generally, roughly classified into a fibrous structure type (ex. sepiolite, attapulgite, etc.), a non-crystal structure type (ex. allophane, etc.), mixed layer structure type (ex. kaolinte, montmorillonite, etc.) and the above layer-structure type. Layer-structure inorganic clay minerals take water molecules into a unit space between the layers, and then swelled. By utilizing this property, the hydrogen peroxide in the bleaching agents is to be held as adhered onto the surfaces of the teeth. In the present invention, the layer-structure inorganic clay minerals, which swell

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multiplicative effects of the titanium dioxide photocatalyst, low concentration of hydrogen peroxide and the thickening agent. That is, titanium oxide generates electrons and positive holes by the light irradiation, then it initiates a chemical reaction with hydrogen peroxide to generate active oxygen. The active oxygen shows significantly stronger oxidative force compared with ozone, therefore, it is able to decompose almost all of organic compounds to carbon dioxide. Further, the bleaching composition applied to tooth surfaces is kept without sagging and enough amounts for bleaching the discolored teeth can be supplied, accordingly the handling as well as the safety is much improved.

[0027] The present invention relates to the bleaching compositions bleaching discolored teeth by applying these on the tooth surfaces and then bleaching it based on the photocatalytic action initiated by light irradiation to the applied area. The bleaching composition is characterized by combining titanium dioxide initiating the photocatalyst action with the light irradiation, the chemical compound generating hydrogen peroxide in a aqueous solution and the thickening agent. The following results are shown, therefore the contribution to esthetic improvement of the teeth by the present invention is significant:

- (1) Considerable improvements of bleaching treatment due to easy application of the bleaching composition on the tooth surfaces,
- (2) It is highly safe due to controlled scattering and/or attaching to the mucous membrane of the solution, and also due to the remarkable bleaching effects through the solution of the low hydrogen peroxide concentration,
- (3) Greatly shortened the bleaching time,
- (4) Remarkable bleaching results, and the like.

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[0028] The present invention is explained by the following examples, however, the present invention is not limitted by the examples.

Examples 1 to 14 and Comparable Example:

(1) Preparation of the bleaching compositions

[0029] Titanium dioxide, a thickening agent, a chemical compound generating hydrogen peroxide in an aqueous solution and distilled water are mixed so as to obtain the bleaching compositions, which are composed of the constituents shown in Table 1, wherein the concentration of the hydrogen peroxide in the bleaching compositions measured by the permanganate titration.

- (2) Bleaching the discolored tooth
- [0030] By using the bleaching compositions obtained above (1), bleaching treatments have done followed the process below:
 - 1) As preliminary arrangements, the plaque, the tartar, the tar and the like are removed from the discolored tooth surface by a using ultrasonic waves scaler.
 - 2) The tooth surface was cleaned by using rubber-cup and etc., and a conventional method and dried.
 - 3) A plain moisture-proofing method is carried out.
 - 4) A bleaching composition prepared above (1) was applied on the tooth surface and followed by irradiation of ultraviolet rays having the wavelength of 350 nm and over.
 - 5) An irradiation time is 5 minutes and the application of the new bleaching composition and irradiation are repeated every time.

[0031] The results are shown in Table 2, wherein the discoloration intensities of the used teeth (extracted) are classified as follows;

- F1: entire crown uniformly colored light yellow, brown and gray with no striations.
- F2 entire crown uniformly colored a deeper shade than F1, with no striations.
- F3: deep gray and bluish gray with striations.
- F4: entire crown discolored to extremely deep purple and grayish purple

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5		hemical	Content (wf%)	5.8	5.8	5.8	5.8	5.8		5.8	5.8	3.2	5.5	2.0		10	15		0.9	5.8		5.8
10		Oxidative Chemica	Туре	H ₂ O ₂	H ₂ O ₂	Sodium perborate	Sodium perborate	H ₂ O ₂		H ₂ O ₂		H_2O_2	H ₂ O ₂		H ₂ O ₂	H ₂ O ₂		H ₂ O ₂				
15		Agent	Content (wt%)	1.8	4.8	89.	1.8	1.8		-	1.8	2.2	2.0	1.6		1.0	3.5		0,1	1 .5		•
20 25		Thickening Agent	Туре	Hectorite	Hectorite	Hectorite	Hectorite	Hectorite		Hectorite	Hectorite	Hectorite	Sepiolite	Montmotillonite		Nacrite	Saponite		Phosphoric acid	Tera-sodium	pyrophosphate	
30	TABLE 1		Content (wt%)	090.0	0.048	090.0	690.0	090'0		090'0	090.0	0:030	0.100	0.500		0.010	0.100		090.0	0.080		0.060
35		Titanium Dioxide	Particle Diameter (nm)	9	180	180	180	35		5	15	15	35	17		9	15		35	15		9
40			Crystal type	Anatase	Anatase	Anatase	Anatase	Rutile	<u>.,</u>	Anatase	Rutile	Rutile	Anatase	Anatase		Anatase	Rutile		Anatase	Rutile	<u>-</u>	Anatase
45 50			Trade Name	TAYCA AMT-100	TAYCA JA-1	TAYCA JA-1	TAYCA JA-1	Ishihara Techno	TTO-55	TAYCA TKS-201	TAYCA MT-150A	TAYCA MT-150A	TAYCA AMT-600	Shouwa	Titanium F6	TAYCA AMT-600	TAYCA AMT-	150A	TAYCA AMT-600	TAYCA AMT-	150A	TAYCA AMT-100
55			.1	Example 1	Example 2	Example 3	Example 4			Example 6	Example 7					Example 11			Example 13	Example 14	-	Comparative Example

TABLE 2

5		The intensity of Initial discoloration	Wavelenght (nm)	Treatment time (min)	The intensity of discoloration after treatment		
	Example 1	F3.0	385	30	F1.5		
	Example 2	F3.5	385	30	F3.0		
	Example 3	F3.5	385	30	F2.5		
10	Example 4	F3.5	385	30	F3.0		
	Example 5	F3.5	385	30	F1.5		
	Example 6	F3.5	385	10	F1.5		
	Example 7	F3.5	385	10	F1.5		
15	Example 8	F3.5	300	20	F2.0		
	Example 9	F3.5	350	60	F2.0		
	Example 10	F3.5	365	60	F3.0		
	Example 11	F3.5	400	60	F3.0 .		
	Example 12	F3.5	385	40	F3.0		
20	Example 13	F3.0	385	15	F2.0		
	Example 14	F3.0	385	15	F1.5		
	Comparative Example	F3.5	385	120	F3.0		

INDUSTRIAL APPLICABILITY

[0032] The present invention relates to the method for bleaching discolored teeth by applying a bleaching composition, which comprises the specified constituents having photocatalytic activity, onto the discolored teeth and then irradiating the applied area with light, and also the present invention relates to tooth bleaching compositions useful for the bleaching method.

Claims

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- A tooth bleaching composition comprising titanium dioxide initiating photocatalytic action with light irradiation, a chemical compound generating hydrogen peroxide in an aqueous solution and a thickening agent.
- The tooth bleaching composition according to claim 1, wherein titanium dioxide is anatase type, rutile type or brookite type.
 - 3. The tooth bleaching composition according to claim 1 or 2, wherein the chemical compound generating hydrogen peroxide in a aqueous solution is selected from the group consisting of hydrogen peroxide, perborate, percarbonate, persulfate, perphosphate, calcium peroxide, magnesium peroxide and urea peroxide.
- 4. The tooth bleaching composition according to claim 3, wherein the chemical compound generating hydrogen peroxide in an aqueous solution is hydrogen peroxide.
- 5. The tooth bleaching composition according to any one of claims 1 to 4, wherein the thickening agent is selected from the group consisting of the layer-structure clay mineral, phosphoric acid and phosphate.
 - 6. The tooth bleaching composition according to any one of claims 1 to 4, wherein the thickening agent is an inorganic clay mineral selected from the group consisted of saponite, montmorillonite, stevensite, hectorite, smecnite, nacrite and sepiolite.
 - 7. The tooth bleaching composition according to claim 5, wherein the phosphate is tetra-sodium pyrophosphate.
 - 8. The tooth bleaching composition according to any one of claims 1 to 7, wherein the content of the chemical com-

pound generating hydrogen peroxide in an aqueous solution is 35 % by weight or less.

- 9. A method for bleaching a discolored tooth comprising applying the bleaching compound described in any one of claims 1 to 8 onto the surface of a discolored tooth and irradiating the applied surface area with light.
- 10. The method according to claim 9, wherein the wavelength of the irradiating light is 300 nm or longer.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP00/04397

A. CLASSIFICATION OF SUBJECT MATTER Int.Cl ⁷ A61K7/20											
According to International Patent Classification (IPC) or to both national classification and IPC											
B. FIELD	S SEARCHED										
	Minimum documentation searched (classification system followed by classification symbols) Int.Cl ⁷ A61K7/00-50										
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched Jitsuyo Shinan Koho 1922-1996 Toroku Jitsuyo Shinan Koho 1994-2000 Kokai Jitsuyo Shinan Koho 1971-2000 Jitsuyo Shinan Toroku Koho 1996-2000											
Electronic data base consulted during the international search (name of data base and, where practicable, search terms used) CAS (STN) REGISTRY (STN)											
C. DOCU	MENTS CONSIDERED TO BE RELEVANT										
Category*	Citation of document, with indication, where ap		Relevant to claim No.								
Y	JP, 11-92351, A (Takuro ISHIBASHI), 1 06 April, 1999 (06.04.99), Full text & WO, 99/15143, Al										
Ā	US, 5032178, A (Demetron Resear 16 July, 1991 (16.07.91), Full text; eapecially, column 1 line 1 & EP, 516872, A & JP, 4-25	1-6,8-10									
Y	JP, 60-75413, A (LION CORPORAT: 27 April, 1985 (27.04.85), Full text (Family: none)	5-6,8-10									
¥	JP, 51-59097, A (Jon Uiriamu Ra 22 May, 1976 (22.05.1971), Full		5-6,8-10								
	r documents are listed in the continuation of Box C.	See patent family annex.									
"A" docume conside "E" earlier date "L" docume cited to special "O" docume means "P" docume docume means "P" docume means "P" docume means "P" docume consideration of the consid	categories of cited documents: ent defining the general state of the art which is not red to be of particular relevance document but published on or after the international filing ent which may throw doubts on priority claim(s) or which is o establish the publication date of another citation or other reason (as specified) ent referring to an oral disclosure, use, exhibition or other ent published prior to the international filing date but later e priority date claimed	priority date and not in conflict with the understand the principle or theory understand the principle or theory understand the principle or theory understand the considered novel or cannot be considered step when the document is taken alone document of particular relevance; the considered to involve an inventive step combined with one or more other such combination being obvious to a person	considered novel or cannot be considered to involve an inventive								
18 5	sectual completion of the international search september, 2000 (18.09.00)	Date of mailing of the international search report 03 October, 2000 (03.10.00)									
	unling address of the ISA/ nese Patent Office	Authorized officer									
Facsimile N	o.	Telephone No.									

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